DISTRIBUTION EQUILIBRIA OF METALS BETWEEN LIQUID ALLOYS AND SALT MELTS IN HIGH TEMPERATURE POLAROGRAPHY

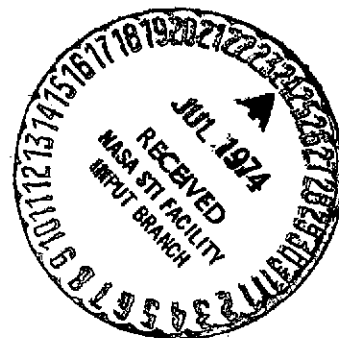## H. Hoff

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16. Abstract

The distribution of Pb, Cd, Mn, Cu and Tl between an electrolyte (NaCl/KCl) and a liquid Ag/Cu alloy has been measured. The concentrations in the salt are partially determined by the reduced activity of the metal in the alloy. The consequences in respect to polarographic investigations in molten chlorides at temperatures above 850° are discussed.

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AND SALT MELTS IN HIGH TEMPERATURE POLAROGRAPHY
H. Hoff

This work is related to the development of a dropping /466*
silver electrode for high temperature polarography [1].
In polarograpy, the measurements of potential, half-wave
potential, $E_{\frac{1}{2}}$, current, and limiting current are linked
together either through the Heyrovsky-Ilkovich relation or
through the Kolthoff-Lingane relation [2].

The Heyrovsky-Ilkovich relation is based on the assumption
that the oxidized species diffuses toward the electrode surface
and the reduced species diffuses away from the surface, either
in the interior of the electrode or in the electrolyte, due
to the solubility of the metal in the fused salt. In this case
the activity of the reduced phase is a function of the current,
while the half-wave potential is a constant. If the activity
of the reduced species can always be set to unity, independent
of the current, then the Kolthoff-Lingane relation applies and
$E_{\frac{1}{2}}$ becomes a function of the concentration of the oxidized phase.

The measurements show that the description of the current-
potential curve is not determined solely by the electrode material
and the oxidized and reduced species, according to the Heyrovsky-
Ilkovich or Kolthoff-Lingane relations, but also by the concen-
trations and the absolute temperature [3].

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* Numbers in margin represent pagination in original foreign text.

When the experimental temperature is raised above 800°C
the question of whether the reduced species must be calculated
with constant or variable activity gains in importance, even
without an externally impressed current:

As is generally common in polarography, the salt dissolved
in the electrolyte is in equilibrium with the metal electrode.
The active processes, such as transport processes and chemical
reactions, proceed considerably faster in comparison to aqueous
polarography. Now we must consider the exchange reaction of the
oxidized species, i. e., of the added salt, with the drop metal.
The concentrations differ sharply depending on whether the
activities of the reduced species are nearly unity, or are
decreased by alloying.

If one designates the dropping metal as M (e. g., Ag) and
the cation of the salt to be investigated as M', with the valence
ν (e. g., $PbCl_2$), then the exchange reaction can be formulated
generally as

$$M'Cl_\nu + \nu M \rightleftharpoons \nu MCl + [M']_{(M)} \cdot \quad (1)$$

Unfortunately, the thermodynamic data for calculating this
distribution equilibrium are only partial and not always known
with the necessary accuracy (see Table 1). In addition they
are often measured only for a certain temperature, so that
extrapolation to the experimental temperature has a large error.
For the salt $M'Cl_\nu$, $PbCl_2$, the decomposition potentials and the
free enthalpies of formation, as measured by various authors,
are given in Table 1.

It appeared advisable, therefore, to determine the
distribution equilibrium for some salts between Ag or an Ag-Cu
alloy and a NaCl/KCl basic electrolyte, so as to be able to

Table 1.

Value (V)	ΔG^0 (kcal) at 850°C	Authors
1,052	−48,50	[5] W. Hamer, M. Malmberg, B. Rubin
1,054	−48,52	[8] R. Lorenz, H. Velde
1,075	−49,50	[9] A. Wachter, I. H. Hildebrand
1,076	−49,51	[10] Steinle, H. Hoff
1,089	−50,20	[11] W. Pfeiffer
1,094	−50,50	[12] M. F. Lantratow, A. F. Alabüschew
1,100	−50,70	[13] O. H. Weber

E^0 is referred to the chlorine electrode at 850°C.

select systems to be considered for polarographic investigations.

Experimental Design

The reaction vessel, in analogy with polarographic investigations, is a carbon crucible of spectrally pure graphite in a quartz tube with ground joint and glass connection. Either the metal or the salt, MCl, can be added through a central quartz tube with a lock. At the same time, this tube serves for argon flushing of the melt. Another quartz tube makes possible removal of electrolyte samples for chemical analysis. The rate of attainment of equilibrium can be followed with a silver wire as the indicator electrode. The reference electrode is a silver wire dipping into a thin-wall quartz tube, sealed at one side, which contains about 0.1% AgCl by weight along with NaCl and KCl as the electrolyte. The Pt/PtRh thermocouple is protected from direct contact with the melt by a quartz tube. Except for the sampling tube, which is sealed to the glass connection with a rubber tube, all the other connections have glass joints. The

potential between the indicator electrode and the reference elect-
rode, as well as the temperature, are plotted with a potentiometric
recorder.

The highest-purity salts of the base electrolyte (NaCl:KCl =
50:50 mole percent) and the metal chloride to be studied are
predried at 200°C for 24-48 hours in a heatable desiccator.
All weighings are done in a glove box under protective gas. The
base electrolyte is fused together in a quartz apparatus under
an atmosphere of HCl. A 24-hour argon wash displaces the dissolved
HCl. Because of its high vapor pressure and the related vapor-
ization loss, the anhydrous metal chloride, $M'Cl_x$, could not be
added to the base electrolyte in pure form. It proved necessary
to produce a concentrate of NaCl, KCl, $M'Cl_x$ with about 10 mole-% $M'Cl_x$
using argon flushing and to determine the exact content of $M'Cl_x$
by chemical analysis. By casting the concentrate in rod form
it was possible to add it to the reaction vessel through the lock
without disturbance.

Performance of the Experiment

The quartz tube with the carbon crucible and the pre-melted
and weighed base electrolyte is heated for 4 hours at 250°C and
10^{-2} Torr and then brought to the experimental temperature in
an argon atmosphere. The work with pure silver was done at 965°C,
and that with a silver-copper alloy (Ag:Cu = 60:40 atom-%), which
is also used in polarographic studies, was done at 850°C. The
adjustments of equilibrium were determined in several experiments
and with different starting conditions. Once the electrolyte,
with the dissolved concentrate of known amount and concentration
of $M'Cl_x$ was added to the metal (see Figure 2). Another time,
the concentrate was added in several portions to the electrolyte
and the liquid metal (see Figures 3 and 4). After attainment of
equilibrium (constant potential between the indicator and the

reference electrode) between the individual additions, electrolyte samples were taken for analytical determination of the salt concentration. The activities could be calculated and the constancy of the activity coefficient in the concentration range studied could be tested by means of the conversion of the reaction, i. e., the decrease in the equivalents of $M'Cl_n$ and the increase of MCl. The equivalents of M' dissolved in M agreed with the decrease of $M'Cl_n$ and the increase of MCl within 4% as a rule. The error is caused essentially through losses in sampling and through evaporation loss of the electrolyte. The slight decrease in the equivalent ion fraction of Figure 2 is explained by the relatively high vapor pressure of $PbCl_2$ at 965°C.

Measurements

The attainment of equilibrium is shown schematically in Figure 1 by means of the change of potential with time. Curve 1 applies for the case in which the concentration equilibration is produced solely by the natural convection within the electrolyte. The time to reach 90% of the steady final value is about 50 seconds. If the mixing is increased by argon flushing (Curve 2) the time is about 20 seconds. Accordingly, the slowest partial step for the attainment of equilibrium is not the chemical reaction but a transport process. Some characteristic concentration-time diagrams are shown in Figures 2 - 4 as examples of the systems measured and listed in Table 2, column 1. Figure 2 shows how the lead content of the salt phase decreases sharply through /468 addition of metallic silver to the electrolyte and how the silver ion content simultaneously rises sharply. With respect to the interesting total conversion in attainment of equilibrium, the equivalent ion fraction of the cation, introduced by Forland [4] was chosen as the ordinate. For M''^+ this is defined as:
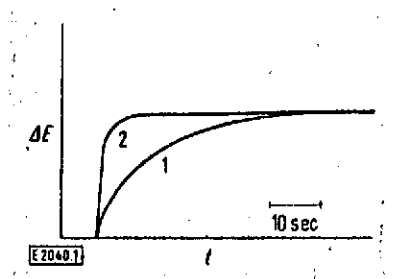
Figure 1. Time change of potential between the Ag indicator
electrode and the encapsulated Ag reference electrode.
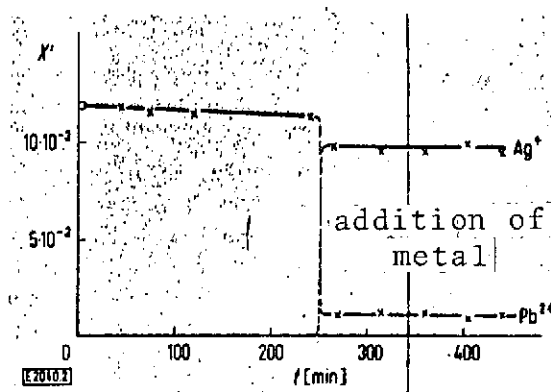1. without; 2. with argon flushing of the electrolyte.

Figure 2. Change of the equivalent ion fractions of Pb^{2+} and
Ag^+ in the electrolyte after addition of Ag (T = 965°C).
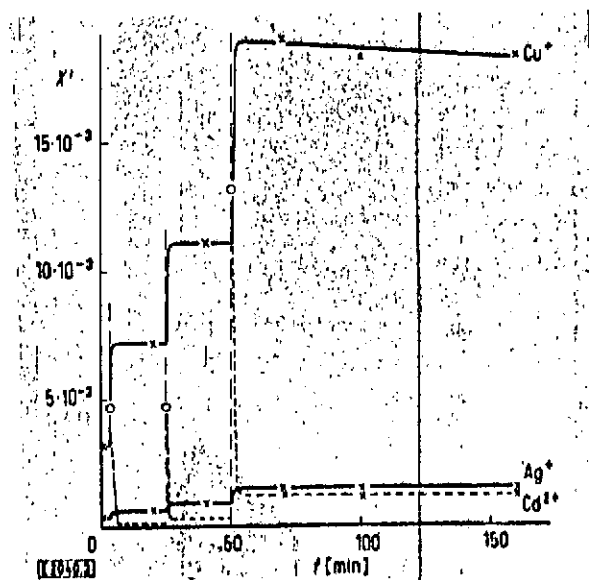
Figure 3.   Rise in concentrations of Cu^+ and Ag^+ on three additions of $CdCl_2$ (T = 850°C).
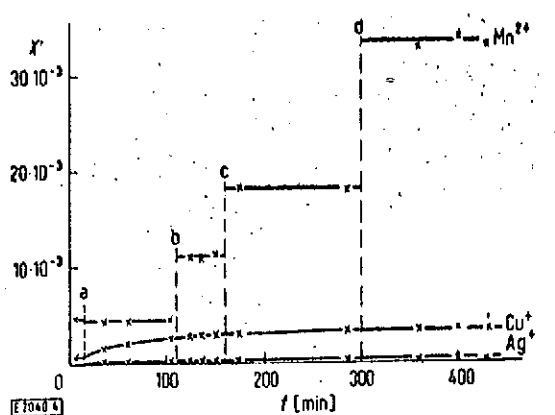

Figure 4.   Equivalent ion fractions in the system $MnCl_2$ dissolved in NaCl/KCl in equilibrium with a Ag/Cu alloy at 850°C.   a) addition of alloy.   b) 2d addition of $MnCl_2$. c) 3rd addition of $MnCl_2$.   d) 4th addition of $MnCl_2$.

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$$X'_{M'} = \frac{\nu \cdot n_{M'}}{\nu \cdot n_{M'} + n_{Na} + n_K + n_{A_R}} \; ;$$

where n is the number of moles of the metal ions.

At 965°C, the ratio of the equivalent ion fractions adjusts
to $X'_{A_R} : X'_{Pb^{2+}} = 9{,}5 : 1$. From the starting weight of the base electro-
lyte and from the amount and the $M'Cl_\nu$ content of the concentrate
we get the theoretical ionic fraction at the time t = 0.
Because of the generally higher partial pressure of the added
salt, compared to the NaCl/KCl mixture, samples were taken at
different time intervals. From the decrease of $X'_{M'}$ a correction
can be calculated, which helps to consider the vaporization
losses in the material balance for the reaction, to a first
approximation. For example, Figure 3 shows, as an example of
attainment of equilibrium of $CdCl_2$ (dissolved in NaCl/KCl) with
the Ag/Cu alloy the stepwise increase in Cu^+ and Ag^+ ions after
three additions of the salt. The initial concentration of $CdCl_2$
before the conversion could be calculated only from the starting
weight. The balance of the three reactions gave a decrease of
$(45 \pm 1) \cdot 10^{-4}$ equivalents of Cd^{2+} and in increase of (44 ± 1)
in Ag^+ and Cu^+ ions. The total Cd content of the alloy was
$(20.5 \pm 1.5) \cdot 10^{-4}$ mole, corresponding to $(41 \pm 3) \cdot 10^{-4}$
equivalents of Cd^{2+}.

In the experiments with $MnCl_2$ (Figure 4), no concentration
change due to the reaction could be detected within the accuracy
of the analysis (2% relative). The analytically determined
equivalent ion fractions agreed with the calculated ones. The
increase in the Cu^+ and Ag^+ ions after addition of the alloy
(Figure 4) is conditioned by the residual water content of the
melt. X'_{Cu^+} was about $3 \cdot 10^{-3}$ to $3.5 \cdot 10^{-3}$ in all the experi-
ments with the Ag/Cu alloy, and X'_{A_R} was $0.25 \cdot 10^{-3}$ to

Table 2.

No.	System	$-E_0$ of the salt volts [3]	γ for the salt [4]	Ratio of ion fractions theor/exp.	$X_{M'Cl_z}/X_{MCl}$ experimental	γ for the metal exp/lit.
1	$PbCl_2 + 2Ag \rightleftharpoons 2AgCl + [Pb]_{(Ag)}$	1,024 0,780	$\gamma_{PbCl} = 0,2$ $\gamma_{AgCl} = 1,00$	$X_{PbCl_2}/(X_{AgCl})^2$ 500 5,5	$5 \cdot 10^{-2}$	$\gamma[Pb]_{(Ag)}$ 1,67 1,9
2	$PbCl_2 + 2[Ag-Cu] \rightleftharpoons 2(AgCl + CuCl) + [Pb]_{(Ag-Cu)}$	1,100 0,810 0,955	$\gamma_{PbCl_2} = 0,18$ $\gamma_{CuCl} = 0,32$	X_{CuCl}/X_{AgCl} 14 12,8 $X_{PbCl_2}/(X_{AgCl})^2$ 2240 114 $X_{PbCl_2}/(X_{CuCl})^2$ 11 0,46	0,12 $0,75 \cdot 10^{-2}$	$\gamma[Ag] = 1,22 \; \gamma[Cu] = 1,67$ $\gamma[Ag] = 1,22 \; \gamma[Cu] = 1,67$ $\gamma[Pb]_{(Ag-Cu)}$ 4,5 3,3
3	$CdCl_2 + 2[Ag-Cu] \rightleftharpoons 2(AgCl + CuCl) + [Cd]_{(Ag-Cu)}$	1,153 0,810 0,955	$\gamma_{CdCl_2} = 0,013$	$X_{CdCl_2}/(X_{AgCl})^2$ 9250 95 $X_{CdCl_2}/(X_{CuCl})^2$ 432 1	0,16 $1,6 \cdot 10^{-2}$	$\gamma[Cd]_{(Ag-Cu)}$ 0,15 0,2
4	$TlCl + [Ag-Cu] \rightleftharpoons (AgCl + CuCl) + [Tl]_{(Ag-Cu)}$	1,432 0,810 0,955	$\gamma_{TlCl} = 1$	X_{TlCl}/X_{AgCl} 675 17 X_{TlCl}/X_{CuCl} 48 1,2	17 1,2	$\gamma[Tl]_{(Ag-Cu)}$ 2,0 —
5	$MnCl_2 + 2[Ag-Cu] \rightleftharpoons 2(AgCl + CuCl) + [Mn]_{(Ag-Cu)}$	1,991 0,810 0,955	$\gamma_{MnCl_2} = 0,0125$	$X_{MnCl_2}/(X_{AgCl})^2$ $3 \cdot 10^{12}$ $2,3 \cdot 10^3$ $X_{MnCl_2}/(X_{CuCl})^2$ $1,6 \cdot 10^9$ $1,1 \cdot 10^3$	120 8,3	$a[Mn]_{(Ag-Cu)}$ $3 \cdot 10^{-7}$
6	$2CuCl + Pb \rightleftharpoons PbCl_2 + [Cu]_{(Pb)}$	+0,955 +1,100	$\gamma_{CuCl} = 0,32$ $\gamma_{PbCl_2} = 0,18$	$(X_{CuCl})^2/X_{PbCl_2}$ 0,11 0,05	2,4	$\gamma[Cu]_{(Pb)}$ 6,6 5,5
7	$2AgCl + Pb \rightleftharpoons PbCl_2 + [Ag]_{(Pb)}$	+0,810 +1,100	$\gamma_{AgCl} = 1$ $\gamma_{PbCl_2} = 0,18$	$(X_{AgCl})^2/X_{PbCl_2}$ $4,5 \cdot 10^{-4}$ $7,6 \cdot 10^{-6}$	$4 \cdot 10^{-3}$	$\gamma[Ag]_{(Pb)}$ 2,5 2,8

$0.3 \cdot 10^{-3}$. The ratio $X'_{Cu^+} : X'_{Ag^+} \approx 12.3$ was not affected by addition of MCl up to several mole-%. That is, the activity coefficients γ_{CuCl} and γ_{AgCl} are determined by the base electrolyte.

Discussion

The equilibrium (1) is described thermodynamically by

$$E^0_{MCl} + \frac{R \cdot T}{v \cdot F} \ln\left(\frac{a_{MCl}}{a_M}\right)^v = E^0_{M'Cl_v} + \frac{R \cdot T}{v \cdot F} \ln\frac{a_{M'Cl_v}}{a M'_{(M)}^v} . \tag{2}$$

This equation can be transformed to

$$E^0_{MCl} - E^0_{M'Cl_v} = \frac{R \cdot T}{v \cdot F}\left(\ln\frac{X_{M'Cl_v}}{(X_{MCl})^v} \right.$$
$$\left. + \ln\frac{\gamma_{M'Cl_v}}{(\gamma_{MCl})^v} - \ln\frac{N_{M'}}{(N_M)^v} - \ln\frac{\gamma_{M'}}{(\gamma_M)^v}\right) ; \tag{3}$$

E^0_{MCl} = standard potential of MCl, referred to the chlorine electrode;

X_i = mole fraction $\left(X_i = \frac{n_i}{\sum n_i}\right)$;

a = activity; γ = activity coefficient; N = atom percent.

The difference in the standard potentials is proportional to a sum of logarithms. The first two terms give the activity ratio of the salts in the solvent NaCl/KCl, while the third and fourth summands describe the activities of the reduced phases. As shown in Table 1 with $PbCl_2$ as an example, the standard potentials cited in the literature already show significant differences. As the activity coefficients (Table 2, column 3) determined by Flengas and Ingraham [6] for a number of salts in NaCl/KCl electrolyte are referred to the thermodynamic data of Hamer, Malmberg and Rubin [5], the E^0 values of those authors are used in the present work (Table 2, column 2).

With respect to the concentration and activity ratios
of interest in polarography, we may make use of Equation (3).
If the Kolthoff-Lingane relation is valid, then with respect to
(3) it means that we can set $N_{M'} \cdot \gamma_{M'} = 1$ and then need consider only
the reduced activity a_{Cu} and a_{Ag} of the alloy (Ag:Cu = 60:40
atom-%). The ratio of ion fractions, $X_{M'Cl_r}/(X_{MCl})^r$ calculated
under this assumption from the standard potentials, as a theor-
etical value, is compared to the experimentally determined ratio
in column 4. The simple fractions $X_{M'Cl_r}/X_{MCl}$ are shown in column 5.

The great discrepancy between the theoretical and experi-
mental values shows that the concentrations in the melt are deter-
mined by the variable activities of the reduced phase in the
metal, M, in opposition to the basis of the Kolthoff-Lingane
relation. From Equation (3) and the measurements we can
calculate the activity coefficients $\gamma_{M'}$ (Table 2, column 6).
The content of M' dissolved in M was about 5 atom-%. The values
are referred to the data cited by Hultgren [7]; that is,
γ_{Ag} = 1.22 and γ_{Cu} = 1.67 (for 850°C) and the ratio of

$\frac{\gamma_{Ag}}{\gamma_{Cu}} = 0.73$ which was confirmed in this work.

The activity coefficients obtained from EMF measurements
by Chondary and Ghosh [15] are γ_{Ag} = 1.23 and γ_{Cu} = 1.60.

For the binary system, the activity coefficients of M'
dissolved in M at the corresponding experimental temperature
can be partially calculated — to the extent that the enthalpies
and entropies of mixing are known — or estimated (shown in
Column 6 as literature values). For the ternary systems (M'
dissolved in Ag/Cu alloy) an approximate value for $\gamma_{M'}$ was
calculated according to a rule suggested by Johnson [14] from
the binary boundary systems.

The results of systems 1 and 2 give rise to the conjecture that Pb might perhaps be a better dropping metal than Ag or a Ag/Cu alloy. Therefore, in system 6, the reaction of CuCl with Pb and in system 7, the reaction of AgCl with Pb were studied. But in these cases, too, the activities of the reduced phases, which differ from unity, makes the concentration ratios poorer with respect to polarography. In the case of $MnCl_2$ as $M'Cl_i$, we can state only a theoretical activity for Mn, because no Mn was found analytically in the alloy.

From the results it can be concluded that it is necessary to consider the changing activity of the reduced phases with the separation. The current-potential relation can be described by the Heyrovsky-Ilkovich equation. The often very small concentration ratio of $\left|\frac{X_{M'Cl_y}}{X_{MCl}}\right|$ means that the measurements are made more difficult by a large background current, due to X_{MCl}. Of the systems investigated, only the experiment with $MnCl_2$ dissolved in NaCl/KCl appears to promise success.

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